

# HYGROSCOPIC STRESS AND FAILURE OF COATING/METAL SYSTEMS

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## Résumé

Le développement de la contrainte dans des revêtements organiques de nature différente sous des conditions humides a été étudié. Les valeurs de contraintes hygroscopiques déterminées sont corrélées avec les résultats obtenus à partir d'autres essais comme la spectroscopie électrochimique d'impédance, l'absorption d'eau, l'adhérence et l'analyse thermique. Le rôle de la contrainte hygroscopique dans la dégradation des revêtements organique est discuté. Il est suggéré que cette contrainte participe à la formation et/ou à l'agrandissement des chemins dans le revêtement organique, facilitant ainsi le transport de l'électrolyte vers le support métallique, ce qui provoque sa corrosion. La compréhension de son action destructive doit contribuer à accroître notre connaissance des facteurs contrôlant la corrosion des métaux peints.

## Abstract

Stress development in various types of organic coatings was determined under wet conditions. The values of hygroscopic stress obtained are correlated with the results of other tests such as electrochemical impedance spectroscopy, water uptake, adhesion, thermal analysis. The role of the hygroscopic stress in organic coating degradation is discussed. It is suggested that this stress participates in formation and/or enlargement of pathways in the coating, which enables the transport of the electrolyte to the metallic substrate provoking its corrosion. The knowledge of its destructive action will enhance our understanding of the controlling factors in corrosion of coated metals.

## INTRODUCTION

The need to continuously improve the protection of metals against corrosion by organic coatings incites a considerable research [1-8]. During years various facets of coating degradation were investigated such as transport of water, oxygen and ions, wet adhesion, electrical aspects, mechanical properties, chemical changes, etc. A variety of methods (e.g. electrochemical, accelerated) were developed to evaluate the corrosion of coated metals, and a number of models describing the mechanisms of coating degradation have been proposed [3,5,9-17].

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Recently a "unified model for the degradation of organic coatings on steel in a neutral electrolyte" was published [18]. This model, based on current knowledge and original work, suggests that the degradation occurs as a result of "the transport of ions through conductive pathways formed by an attack by water in the hydrophilic, low-molecular weight/low-crosslinked regions, followed by the connections of these regions". Therefore, the presence of water in the coating appears to be one of the conditions leading to the corrosion of the metal substrate [19,20a].

On the other hand, different aspects of the effect of stresses, e.g. internal (due to film formation) or hygrothermal (due to changes in environmental conditions) on the coating performance were also discussed in the literature. When a high stress develops in a coating, its adhesion can be affected, leading to coating detachment from the substrate [21]. A high stress, alone or in combination with a fatigue process, is also responsible for the cracking of coatings during their exposure to natural or accelerated weathering [22,23]. Also a possible participation of the stress in the failure of coating/metal systems has been discussed in several studies [12,18,24], although no direct proof was provided. On the other hand, it has been shown that a substantial hygroscopic compressive stress can develop in a coating immersed in water or under wet conditions [25].

The aim of this paper is to examine the role of the hygroscopic compressive stress in the failure of coating/metal systems. AC-impedance was measured and used in this work as a means to follow the coating degradation. Their change with aging is an indication of coating diminishing protective efficiency.

## EXPERIMENTAL

### Materials

The coatings investigated were :

- a thermoplastic binder based on polyisobutyl methacrylate (Plexigum)\*,
- a high  $T_g$  acrylic latex,
- an epoxy/polyamide system,
- a polyurethane, and
- a carboxyl-functional poly(ester)/triglycidyl isocyanurate powder coating.

Tin plates, stainless steel calibrated shims, and cold rolled steel panels (QD-36)\* were used as substrates for free films preparation, stress and AC-Impedance measurements, respectively.

All coatings, except the powder coating, were applied with a doctor blade at ambient temperature (21°C, 50 % RH) on various substrates previously degreased by immersing and cleansing in a 50/50 by volume mixture of isopropanol and toluene, followed by drying with hot dry air. Except for

powder coating, other coatings were cured following the manufacturer's recommended schedules. After curing, they were placed in a 50°C air-circulated oven for 24 hours. The powder coating was applied electrostatically and cured for 10 minutes at 190°C. All the tests started after a minimum 1 month conditioning at 21°C and 50% RH.

## Methods

*Stress measurement.* These measurements were made with an apparatus [26] that registers the deflection of a coated substrate induced by the stress. The determination of this deflection and the knowledge of the elastic properties of the substrate permit the calculation of the stress.

*Electrochemical impedance measurement.* Alternative current (AC)-impedance spectra were obtained with the help of a frequency response analyzer (Solartron 1260, Schlumberger)\*. The voltage applied, the cell circular area and the electrolyte used were 10 mV, 706.5 mm<sup>2</sup> and 0.5 M NaCl, respectively. Frequency sweeps from 0.1 to 100 KHz were applied. More complete experimental details are described in reference [20b].

*Water uptake.* These tests were performed gravimetrically at 21°C with free films by immersing the specimens in water, periodically removing, blotting excess water and weighing immediately, until an apparent stationary state was obtained.

*Adhesion.* These measurements consist of attaching a tape to a scored, coated substrate previously exposed to water, cleaning superficial water, and then detaching it at an angle of 180° in an Instron apparatus at a crosshead speed of 100 mm/min. [25a].

*Glass transition temperature ( $T_g$ ).* Mid  $T_g$ -values under dry and wet conditions were determined with a differential scanning calorimeter (Mettler DSC 30)\* at a heating rate of 20°C/min. Since the coatings investigated are subjected to physical aging, as indicated by the presence of an endothermal peak in the  $T_g$ -region (enthalpy relaxation) during the first temperature scan, the  $T_g$  has to be evaluated from the second temperature scan. However, in this study, in order to minimize water evaporation from the specimen, the wet  $T_g$  was determined from the first temperature scan.

## RESULTS

The results of stress, AC-impedance, water uptake, adhesion, and  $T_g$  are presented in figures 1 to 4 and Tables 1 and 2.

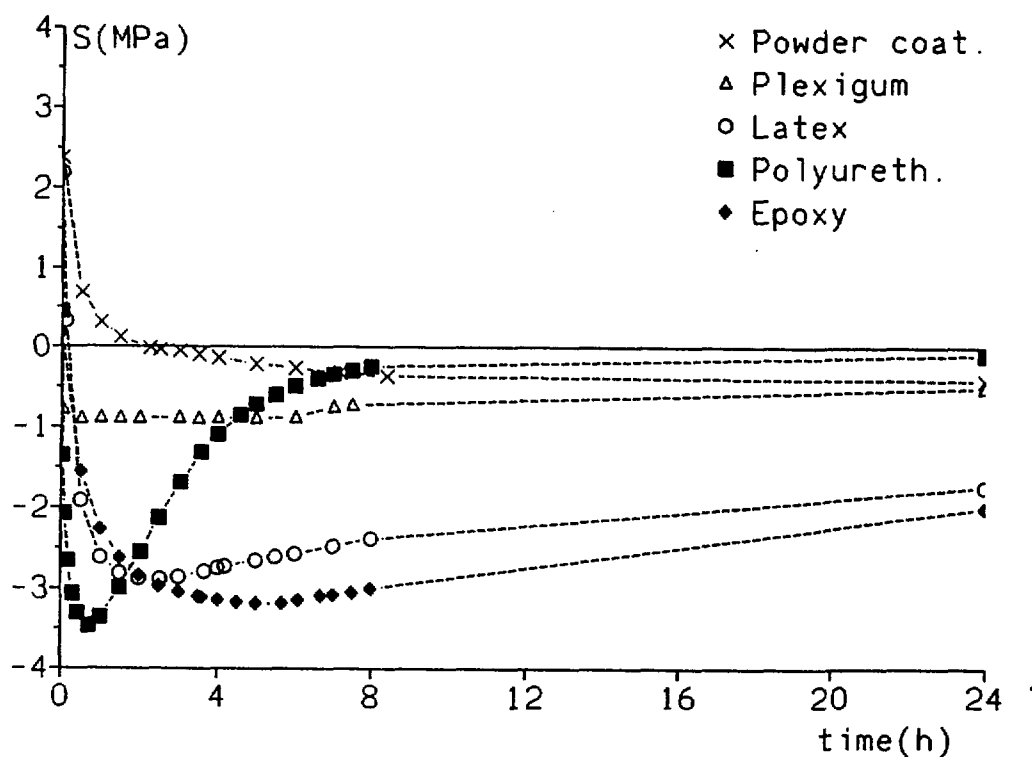


Figure 1. Stress (S) dependence on time (hour,h) at 21°C for the coatings investigated.

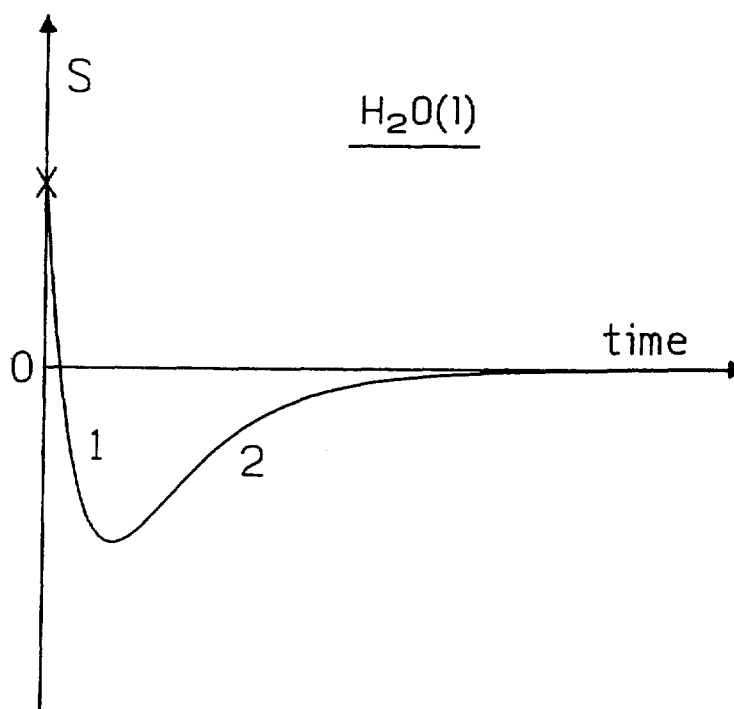


Figure 2. Schematic illustration of stress (S) dependence on time (t) for a coating immersed in water.

## Stress

The stress results obtained with the five coatings are presented in figure 1. An analysis of these results suggest that the stress dependence on time can schematically be illustrated by figure 2.

The development of stress in a coating during its immersion in water can be understood by considering the mathematical relationship describing the hygrothermal stress ( $S^H$ ):

$$S^H = \int_{RH_1}^{RH_2} \frac{E_F (\alpha_F^H - \alpha_S^H)}{1 - \nu_F} dRH \quad (1)$$

where  $E_F$  = elastic modulus of the coating, [Pa]  
 $\alpha_F^H, \alpha_S^H$  = hygroscopic expansion coefficients of the coating and of the substrate, respectively, [ $RH^{-1}$ ]  
 $\nu_F$  = Poisson's ratio of the coating, [-]

In our experiments, the substrate (steel) is not submitted to dimensional changes, i.e.,  $\alpha_S^H = 0$ . Further,  $\alpha_F^H$  is assumed to be due to water taken up by an isotropic coating. Under these conditions, equation 1 becomes:

$$S^H = \int_{RH_1}^{RH_2} \frac{E_F \alpha_F^H}{1 - \nu_F} dRH \approx \frac{E_F \alpha_F^H}{1 - \nu_F} \Delta RH \quad (2)$$

$$where \quad \alpha_F^H = \frac{1}{3} \left( \frac{V_{water}}{V} \right) \frac{1}{RH} \quad (3)$$

where  $V_{water}$  = volume of water taken up by the coating at the corresponding RH  
 $V$  = film volume

Figures 1 and 2 clearly show that the immersion of a coated substrate in water induces a hygroscopic compressive stress (arbitrarily presented as negative values) which, after a period of time, starts to decrease. This change of stress as a function of immersion time can be explained on the basis of the above equations, by considering the way the three coating parameters, i.e. elastic modulus, hygroscopic expansion coefficient, and Poisson's ratio, interact.

Based on the present knowledge, one can assume that, with water uptake,  $\alpha_F^H$  always increases and  $E_F$  decreases if water behaves as a plasticizer (which is the prevalent situation). The effect of  $v_F$  (about 0.4), which generally increases with an increase of water uptake (to about 0.45), is negligible. As a result, the stress will increase or decrease according to the property dominating the process at that time.

The stress rising (see curve 1 in Fig.2) is mainly due to the fact that in this period of time, the increase of  $\alpha_F^H$  exceeds the decrease of  $E_F$ , while the stress decrease (curve 2 in Fig.2) indicates that now the opposite occurs. If no delamination occurs, the stress reduction was shown to be mainly due to relaxation/relief processes, which cause a decrease of  $E_F$ . The relaxation rate is dependent on the real  $T_g$  of the coating once immersed in water; this  $T_g$  can be different from the one usually determined under dry conditions (see Table 1). The higher the  $T_g$  with respect to the experimental temperature, the slower is the relaxation process.

| <b>TABLE 1 : Approximate <math>T_g</math>-values under dry and wet conditions</b> |                               |  |  |
|---|-------------------------------|--|--|
|   | <b>Immersion time (hours)</b> | <b><math>T_{g\text{-wet}}</math> (<math>^{\circ}\text{C}</math>)</b> | <b><math>T_{g\text{-dry}}</math> (<math>^{\circ}\text{C}</math>)</b> |
| Polyurethane  | 0.5                           | 34 $\leq$  | 54   |
|   | 4.0                           | 27 $\leq$  |  |
| Epoxy   | 5                             | 41 $\leq$  | 58   |
| Latex   | 3                             | 42 $\leq$  | 60   |
| Powder coating  | 72                            | 50 $\leq$  | 73   |
| Plexigum  | -                             | -  | 55   |

With respect to the coatings investigated, figure 1 shows that powder coating possesses the lowest hygroscopic compressive stress while latex and epoxy the highest stress. The polyurethane develops a high hygroscopic compressive stress, which relaxes relatively fast.

### **Water uptake**

The water uptake values are presented in figure 3. It shows that the polyurethane has the greatest affinity for water while Plexigum takes up the least amount of water. The order of water uptake in coatings is as follows :

Polyurethane > Latex > Epoxy > Powder Coating > Plexigum

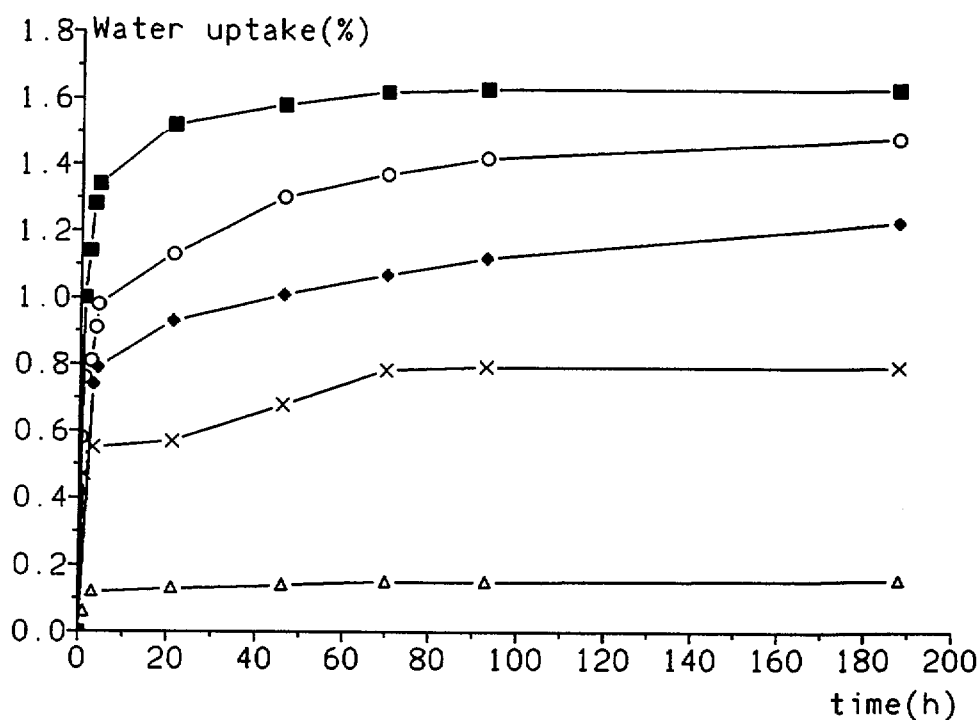


Figure 3. Water uptake as a function of time (hour,h) for the coatings investigated: polyurethane (■), latex (○), epoxy (◆), powder coating (X), Plexigum (Δ).

### Adhesion

The adhesion results presented in Table 2 are those obtained with the coating applied to stainless steel substrates used in the stress measurements. A few adhesion tests were also made with the coatings applied to cold rolled steel panels (used in electrochemical tests) but, since the results are similar with those shown in Table 2, they are not presented in this paper.

The main reason the adhesion tests were carried out is to ensure that the adhesion strength, while decreasing with immersion time, does not reach zero. The results obtained confirm that the decrease in stress (curve 2 in Fig.2) is mainly due to relaxation processes.

### AC-Impedance

The electrochemical test results, namely the Bode Plots (impedance module,  $|Z|$ , as a function of frequency) after various immersion times, are shown in figures 4A to 4D. High values of  $|Z|$ , above  $10^7 \Omega \cdot \text{cm}^2$ , at low frequencies is generally associated with coating capability to insulate a metallic substrate against the damaging effect of the electrolyte [8].

**TABLE 2 : Mean adhesive strength (Peeling, N/m, A) and type of failure (B) for the coatings investigated : polyurethane (PU), Epoxy (Ep), Latex (L), Plexigum (Plex) and Powder Coating (PC)**

|    | PU  |     | Ep  |     | L   |     | Plex |     | PC  |     |
|----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|
| t  | A   | B   | A   | B   | A   | B   | A    | B   | A   | B   |
| 0  | 370 | T/C | 480 | T/C | 380 | T/C | 310  | C/S | 380 | T/C |
| 1h | 350 | T/C | 100 | C/S | 70  | C/S | 10   | C/S | 380 | T/C |
| 1d | 84  | C/S | 60  | C/S | 20  | C/S | 10   | C/S | 360 | T/C |
| 3d | 64  | C/S | 40  | C/S | 20  | C/S | 10   | C/S | 340 | T/C |

Type of failure (B) : T/C = adhesive between tape and coating  
C/S = adhesive between coating and substrate

The results obtained show that  $|Z|$ -values of the

- Powder Coating, and to a lesser extent those of Plexigum, remain high even after 20 days of immersion in 0.5 M NaCl,
- Epoxy and Latex become low after 1 day of immersion (for Latex already after 3 hours of immersion), and
- Polyurethane are in the middle of these two groups.

## Panel Degradation

After 20 days of immersion in 0.5 M NaCl, the general aspect of coated steel samples is as follows :

- Latex is highly corroded,
- Epoxy presents many large black pittings,
- Polyurethane has many small black pittings,
- Plexigum has a few black pittings, and
- Powder coating is not damaged at all.

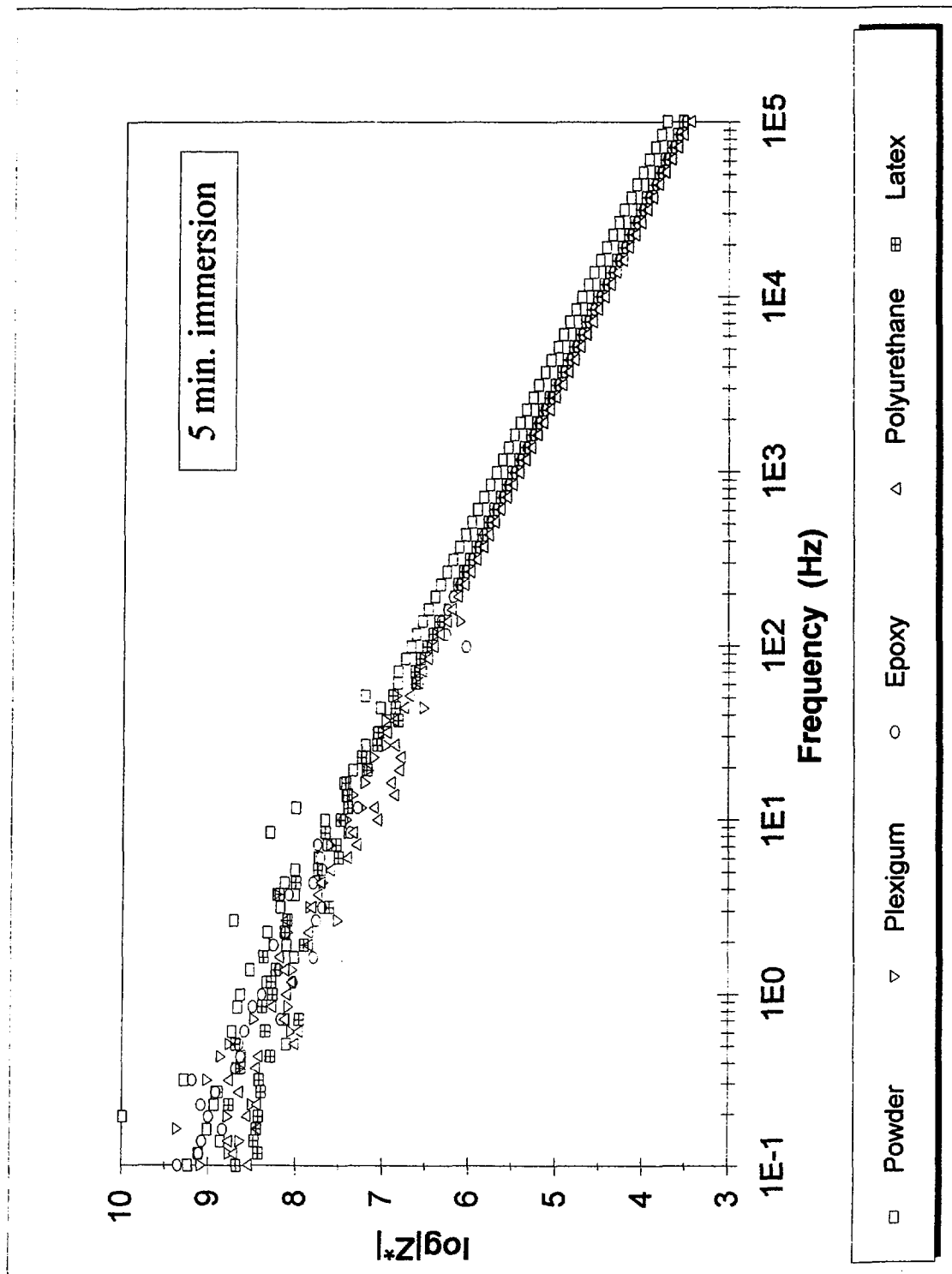


Figure 4A. Impedance module,  $|Z|$ , as a function of frequency for the coatings investigated after 5 minutes of immersion.

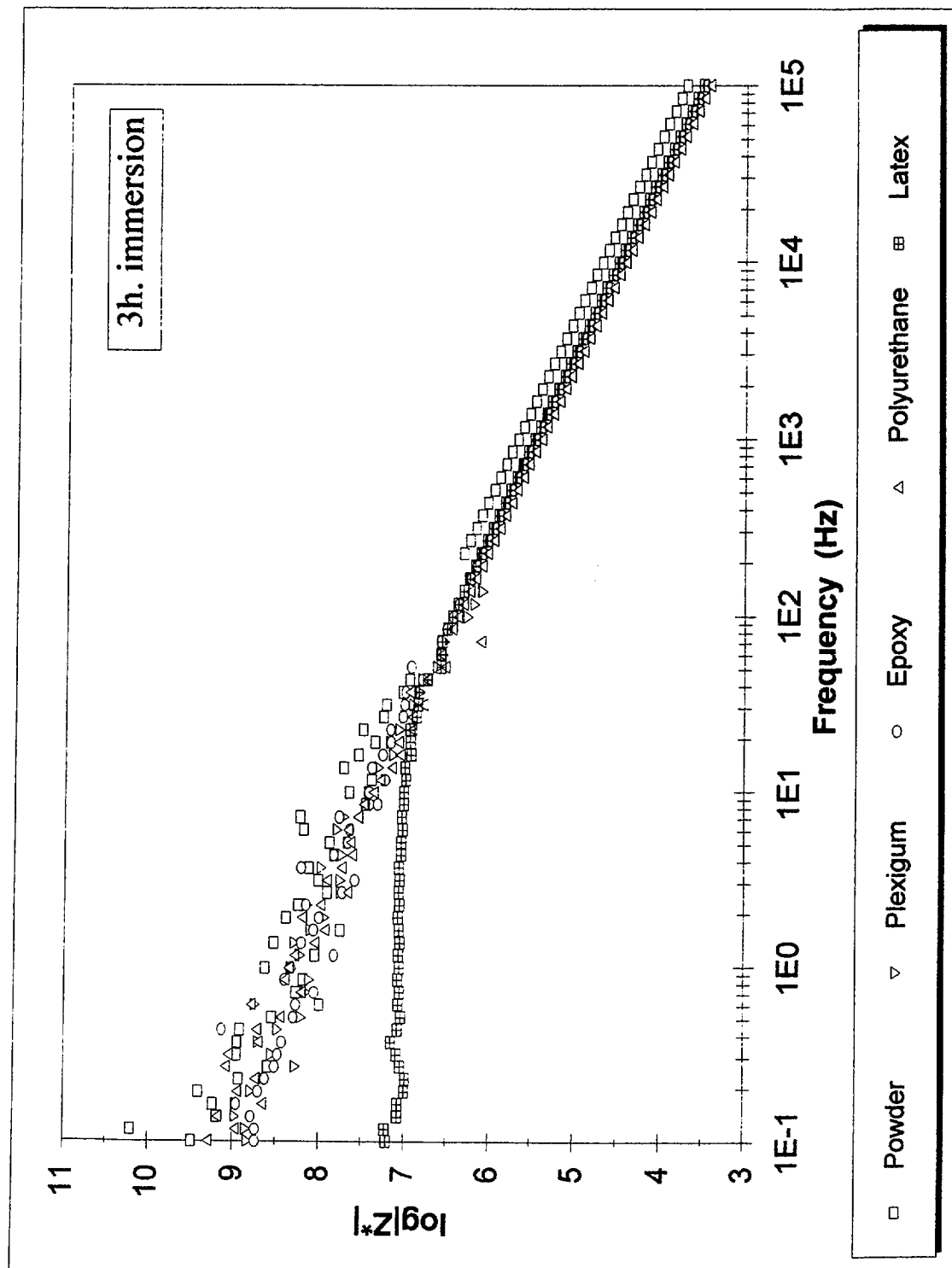


Figure 4B. Idem Figure 4A but after 3 hours immersion.

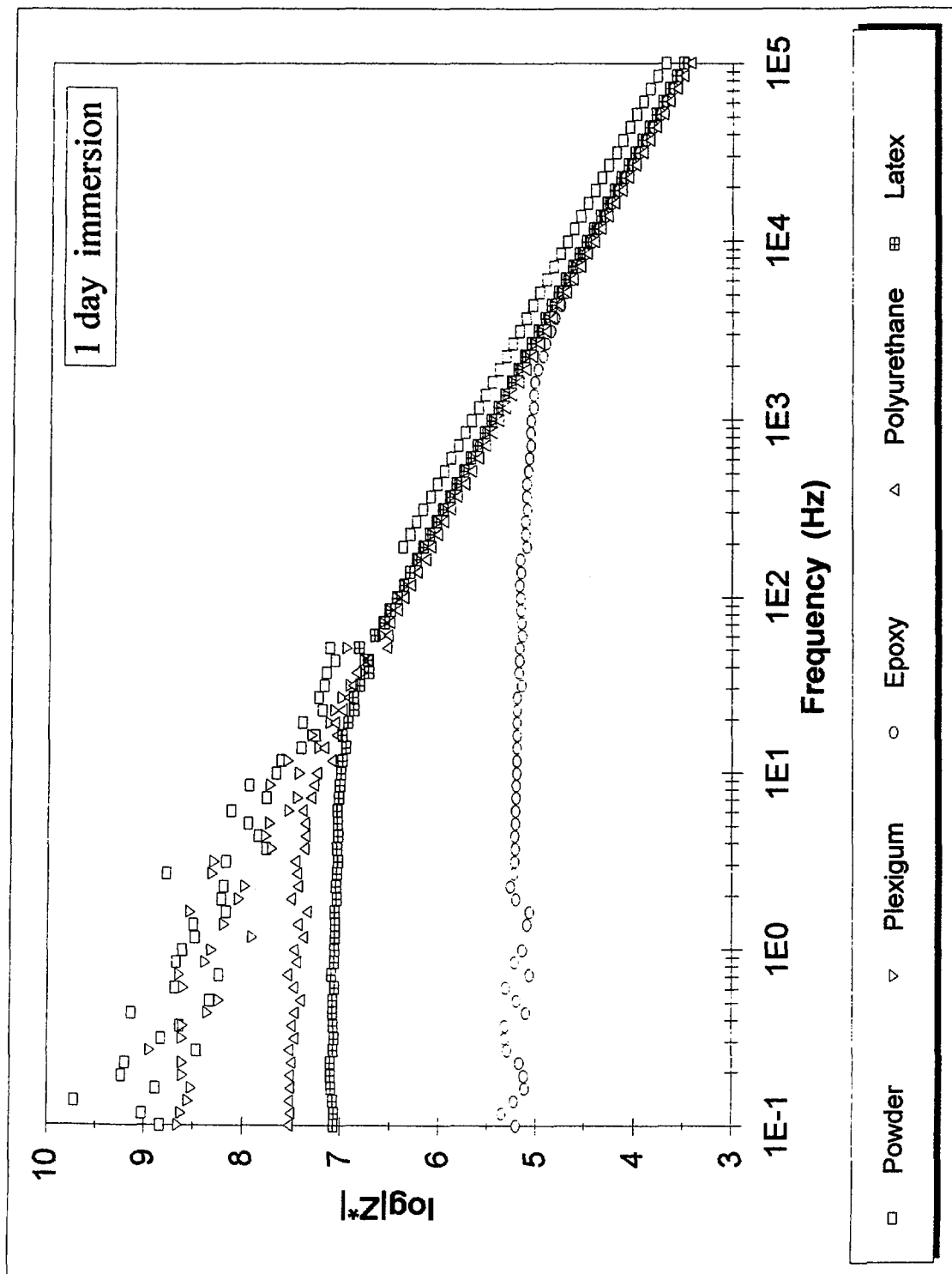


Figure 4C. Idem Figure 4A but after 1 day immersion.

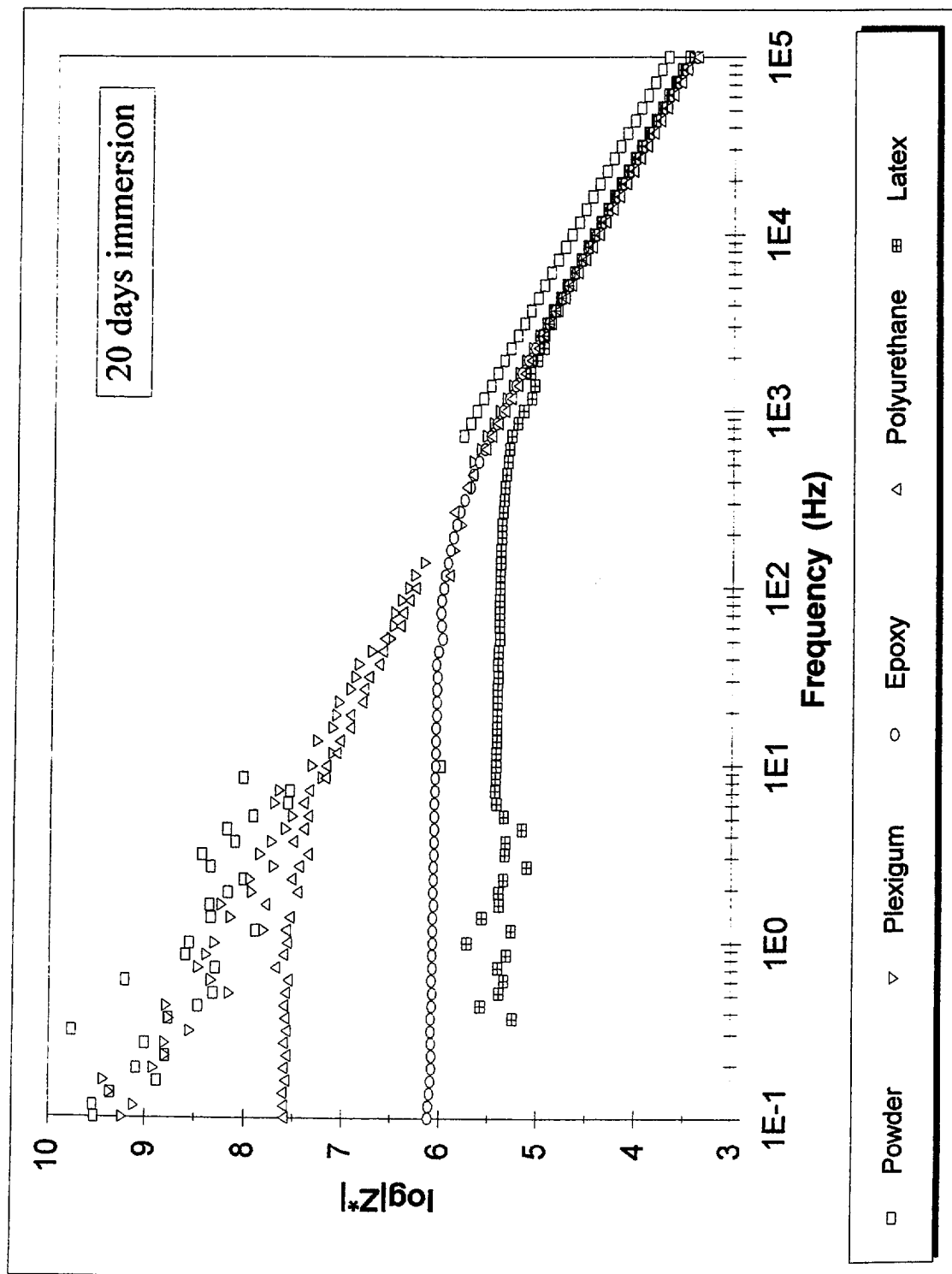


Figure 4D. Idem Figure 4A but after 20 days immersion.

## DISCUSSION

The analysis of the overall results indicates that:

- 1) there is no satisfactory correlation between the amount of water uptake and the performance of coatings as illustrated by the behaviour of the powder coating and polyurethane. The powder coating, which protects efficiently the substrate during the entire immersion period, is not the coating that sorbs the lowest amount of water. The polyurethane, which takes up the highest amount of water, behaves better than the epoxy and the latex, which take up less water.
- 2) there is no direct correlation between the AC-Impedance and wet adhesion as the case of Plexigum shows. This coating, which has a relatively poor bonding to its substrate, possesses high  $|Z|$ -values even after a long period of immersion,
- 3) there is a good correlation between the development of hygroscopic compressive stress and AC-Impedance values. The powder coating, which develops the lowest hygroscopic compressive stress, possesses the highest  $|Z|$ -values. To a less extent this is also valid for Plexigum. Epoxy and latex, which develop a high hygroscopic compressive stress during immersion, induce low  $|Z|$  values and degrade fast.

The case of polyurethane is interesting since it demonstrates that a coating, which initially develops a very high hygroscopic compressive stress (and has a high water uptake), can have a satisfactory behavior if this stress relaxes during a relatively short period of time (see Fig.1). We relate this relaxation to the plasticizing effect of sorbed water which, in the case of polyurethane, brings the  $T_g$  (about 27°C) close to the experimental temperature (about 21.5°C)(see Table 1 and reference [25a]).

The above results also address the question about the influence of the type of sorbed water (strongly bounded, free) on the coating performance. The higher the proportion of the strongly bound water (to coating polar groups) the higher will be the water plasticizing effect and the lower the proportion of free water. The first effect induces a decrease of  $T_g$  enabling the stress to relax, while the second one causes a decrease in ions mobility.

Another coating which deserves a comment is Plexigum. This coating keeps high  $|Z|$ -values during immersion despite its low (wet) adhesion, indicating that AC-Impedance measurements are only related to the insulating efficiency of the coating.

The good correlation found between the values of AC-Impedance and hygroscopic compressive stress indicates that the stress contribution to coating degradation can be significant. The heterogeneous nature of the coating which contains regions of various nature and different degree of hydrophilicity, is at the origin of local stresses developing in an organic coating immersed in water or exposed to a high relative humidity. This is probably a consequence of a difference in the swelling between the hydrophilic and hydrophobic regions, due to their unequal water uptake. We suggest that these hygroscopic local stresses contribute to the enlargement of pathways providing the passage of the electrolyte to reach the substrate, in agreement with the unified model mentioned before.

## CONCLUSIONS

The immersion of a coating in water or its exposure to a high relative humidity induces the development of hygroscopic compressive stress in the coating. The cause provoking this stress, as well as its evolution with time, was explained in terms of coating properties (elastic modulus, hygroscopic expansion coefficient, Poisson's ratio) determining the stress and the way they are affected by sorbed water and the relaxation process.

The good correlation between AC-Impedance and stress values indicates that the presence of a high stress contributes to coating degradation. Such a stress participates in formation and/or enlargements of pathways in the coating, which enables the transport of the electrolyte to the metallic substrate provoking its corrosion.

The consideration of the stress as a potential factor among those already known (e.g. water attack in the hydrophilic regions) will enhance our capability to develop more effective protective organic coatings for metallic substrates.

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**Keywords:** Coating, Stress, Hygroscopic, Corrosion, Degradation.

\*-Trade names given in this paper are to indicate experimental materials and equipment and are not meant to recommend a particular product by the Coatings Research Institute and the National Institute of Standards and Technology or to imply that they are the best available for the experiment.